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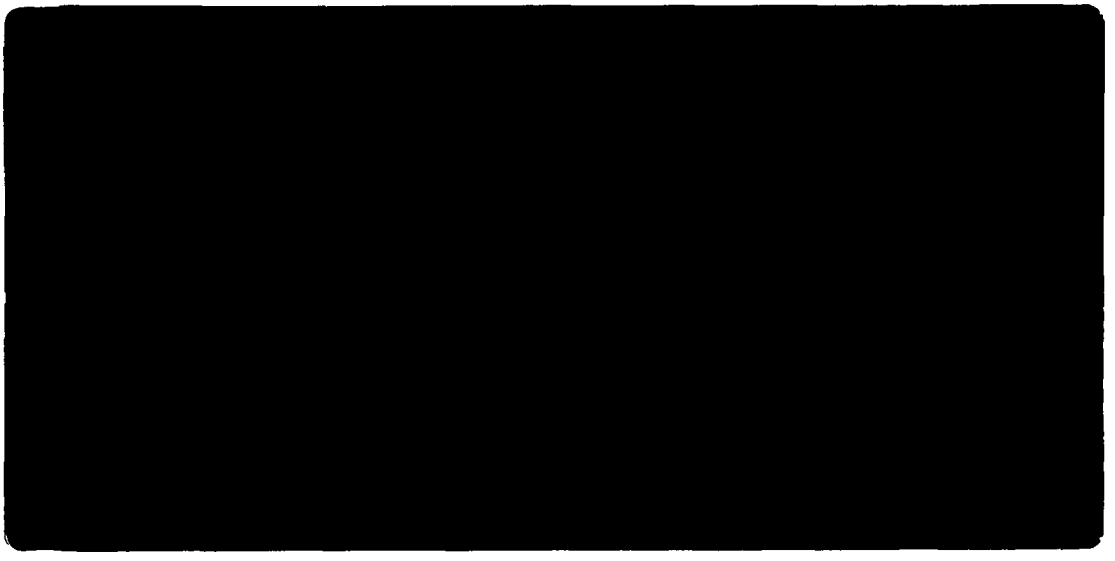

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BLEACHING SCENARIOS FOR THE YEAR 2000

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Bleaching Scenarios for the Year 2000

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ABSTRACT

Various driving forces and resistances will interact to determine the nature of the bleach plant of the year 2000. The most prominent among these are regulatory and market pressures on environmental parameters on one hand and economic realities on the other. AOX, although not useful as a predictor of environmental impact, is a parameter that will very probably have a strong influence on future bleaching process choices. Several technologies are available to reduce AOX, and cost considerations aside, they can be combined in various ways to give more or less additive effects. These technologies are reviewed, with emphasis on the developing ones. Several scenarios for the year 2000 are then developed on the basis of varying assumptions concerning allowable AOX levels. If AOX is limited to a value of 1.5 kg/t, a variety of options are available, all involving replacement of chlorine with chlorine dioxide to an extent depending on the extent to which other technologies are also used. More severe limitations on AOX will further limit the available options. Complete prohibition of the use of chlorine compounds would force a reduction in bleached pulp quality standards and increased production costs.

INTRODUCTION

With a total capacity of more than 50 million tons per year, kraft bleach plants represent both a large installed capital base and an important component of the industry's technology. In addition, bleaching is now commanding considerable attention, as a result of its well publicized potential for environmental effects and the current remarkable growth in consumer concern for the environment. These are but two of a complex set of driving forces and resistances prevailing during a period of unprecedented change in pulp bleaching technology. Collectively, they make it nearly certain that, by the end of the decade and the century, the bleaching processes in use will differ markedly from those of today. The purpose of this paper is to look ahead to that time and make some informed guesses as to the nature of the changes that will occur.

Driving Forces for Change

Clearly, the most compelling forces for change are rooted in concern for the environment. This concern has arisen from the recognition that industries and governments have made mistakes in

the past. Unfortunately, well-intentioned reaction to the effects of these mistakes is sometimes poorly informed and therefore inappropriate. Nevertheless, it will result in irresistible regulatory and market pressures on the industry to alter its technology.

The environmental forces are not the only ones likely to affect the outcome of current technological trends. The need to conserve energy will influence the choice of bleaching chemicals and process conditions. Growing product specialization will have an effect, since the bleaching step represents the major opportunity for chemically modifying fiber properties. Advances in sensors, computers, and process models will enable the use of previously infeasible bleaching methods. Rapid progress in biotechnology will offer new alternatives to the traditional bleaching chemicals. In spite of the potential importance of these forces, however, it is unlikely that any of them will either supersede or operate independently of environmental pressures. Advances in biotechnology and process control, for example, offer opportunities for responding to environmental needs, and energy considerations will play a role in the development of such control technologies as bleach effluent recycling by concentration and burning.

Countervailing Forces

The forces opposing change arise from uncertainty and quality issues. Because of the general complexity of multistage bleaching operations, existing bleach plants represent a very large capital investment with a correspondingly large replacement cost. This factor will favor trends that do not require radical equipment changes. Similarly, operating cost considerations mitigate against the use of large amounts of such expensive chemicals as ozone. They will also slow the transition from chlorine dioxide-chlorine mixtures to the relatively inefficient alternative of using pure chlorine dioxide. Uncertainties regarding the effectiveness of commercially unproven technologies are a barrier to their use. Uncertainty regarding the true value of the benefits that will accrue from expensive new technology similarly provide just cause for caution. Why, for example, invest large amounts of capital to eliminate the last traces of dioxin from an effluent, while new evidence is accumulating that at these low levels they are completely innocuous?

The changes that will result from the interplay between these driving forces and resistances are difficult to predict. We are in the midst of a period of unprecedented global economic and social change, and similarly, unprecedented technological changes may reasonably be expected. Thus, it has been widely predicted that chlorine use will be entirely discontinued in the very near future and that chlorine dioxide's demise will not be far behind. Such predictions gain credibility when it is realized that market pressures for nonchlorine bleaching outweigh the corresponding regulatory pressures, real though the latter may be. This is largely due to the success of environmental activist organizations in swaying public opinion to their point of view.

On the other hand, economics is a powerful force, public opinion is notoriously changeable, and the magnitude of the current trends is sometimes overstated. The American Paper Institute estimates that in 1994 the U.S. industry will continue to consume elemental chlorine at the rate of more than 2500 tons per day[1]. Although this is considerably lower than the nearly 4000 tons

per day used in 1989 and represents an attrition rate of 9% per year, continued attrition at the same rate would see us using 1400 tons of chlorine per day in the year 2000. Chlorine dioxide, now enjoying substantial growth at chlorine's expense, will become vulnerable only if public pressure for totally chlorine-free bleaching strengthens considerably (and the market accepts the resulting loss in product quality) or if a suitable alternative can be found. As of now, no alternative is on the horizon, and the frequently cited market for pulp bleached without chlorine compounds is still small. The total world output of market pulp in 1990 was 34 million tons, of which 23.5 million tons was bleached kraft[2]. The total market in 1991 for pulp bleached without chlorine compounds for use in fine paper was 1.7 million tons, of which less than 0.1 million tons was kraft[3].

AOX as a Criterion for Technology Selection

The selection of bleaching alternatives is strongly influenced by effluent regulations. Until relatively recently, the most frequently regulated parameters were total suspended solids (TSS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), and pH. Adsorbable organic halides (AOX) has been or will soon be added to the list in many jurisdictions. This is unfortunate, because AOX is an unsatisfactory parameter upon which to base regulations. The reason is that it reflects the totality of organically bound chlorine without differentiating between potentially harmful chlorinated organic compounds and innocuous ones. Not all AOX compounds are toxic, as shown by the natural occurrence of AOX in areas of high biological activity[4] and the lack of any observable harmful effects of the significant quantities of AOX in municipally chlorinated drinking water. Furthermore, despite numerous attempts, no correlation has been detected between AOX and toxicity, either acute or chronic[5].

Nevertheless, continued use of AOX as a basis for regulations appears likely. The reasons are the extreme complexity of the mixture of chlorinated organic compounds in bleaching effluents and the relative simplicity of the analytical methodology for measuring AOX. Until the industry can identify an alternative and convince the regulating agencies of its appropriateness, the amount of AOX discharged from a bleach plant will remain a criterion for technology selection.

Other parameters may also become limiting in certain cases. It is almost certain that AOX regulations will be supplemented by regulation of specific compounds, of which one will be chloroform. Since chloroform is generated in hypochlorite stages and, to a lesser extent during chlorination, this will probably result in the elimination of hypochlorite stages and may influence the choice of process conditions for stages employing mixtures of chlorine and chlorine dioxide.

In what follows, an attempt will be made to depict scenarios for bleaching processes likely to be in place at the beginning of the new century. The processes will encompass component technologies that can be put together in various ways, so these are first reviewed individually. Probable combinations are then suggested under each of several alternative sets of assumptions that define the regulatory climate and market pressures that will prevail.

TRENDS IN BLEACHING TECHNOLOGY

Most of the technology that will be common in the bleach plant at the beginning of the century will be quite different from what is now in widespread use. On the other hand, much of it is now available or under development. Oxygen delignification, already becoming commonplace, will be found in the majority of mills, the exceptions being largely confined to hardwood lines and lines employing extended delignification in the digester. Chlorination stages will be replaced with chlorine dioxide delignification stages or will employ mixtures in which chlorine dioxide predominates over chlorine. The use of oxygen in the first caustic extraction stage will be virtually universal and hydrogen peroxide will be used to a considerably greater extent than now. Chlorine dioxide will be extensively used for both delignification and brightening. Greater attention will be paid to washing of brownstock and postoxygen washing, with some mills installing open wash stages. Some newer technologies will have become fully commercialized and will have made significant inroads. These include enzyme pretreatments, ozone bleaching, posttreatment of effluents to dechlorinate organics, and recovery of bleaching effluents.

Relevant technologies are briefly reviewed below, with emphasis on the newer ones. Symbols are assigned to each for convenience in describing sequences. TABLE 1 defines these symbols.

Extended Delignification

Although not a bleaching technology, removal of more lignin in the digester must be mentioned first, since it represents the most desirable solution to problems associated with lignin removal in the bleach plant. The degree to which it can be practiced is constrained by pulp yield and quality requirements and has been increased by the introduction in recent years of several modifications to kraft pulping technology. These include control of liquor concentration profiles in continuous digesters and corresponding liquor displacement sequences and modified chip discharge in batch digesters. Significant reductions in unbleached lignin content are achievable, perhaps comparable to what can be attained by oxygen delignification of a conventional unbleached pulp.

Oxygen Predelignification

Oxygen predelignification (**Figure 1**) allows a major reduction in the use of chlorine and chlorine dioxide for delignification in subsequent stages. This, in turn, markedly decreases the rate of formation of chlorinated organic byproducts, measured as AOX. Additional incentive comes from its beneficial effects on COD, BOD, and color, all of which are reduced in rough proportion to the amount of lignin removed from the pulp, provided that post oxygen washing is very good. The filtrate from this washing stage contains the lignin removed in the oxygen stage and is recycled to the pulp mill's chemical recovery system after being used to wash the entering pulp. In medium consistency systems, about 35-40% lignin removal can be achieved in a single stage or about 50% in a two-stage system with an intermediate mixer. In high consistency systems,

higher degrees of delignification are achievable but are not generally sought because of the potential for pulp strength loss. Greater degrees of lignin removal without strength loss are possible if the unbleached pulp is pretreated with nitrogen dioxide (the "Prenox® Process"), but this shows no signs of being commercialized following pilot trials completed several years ago.

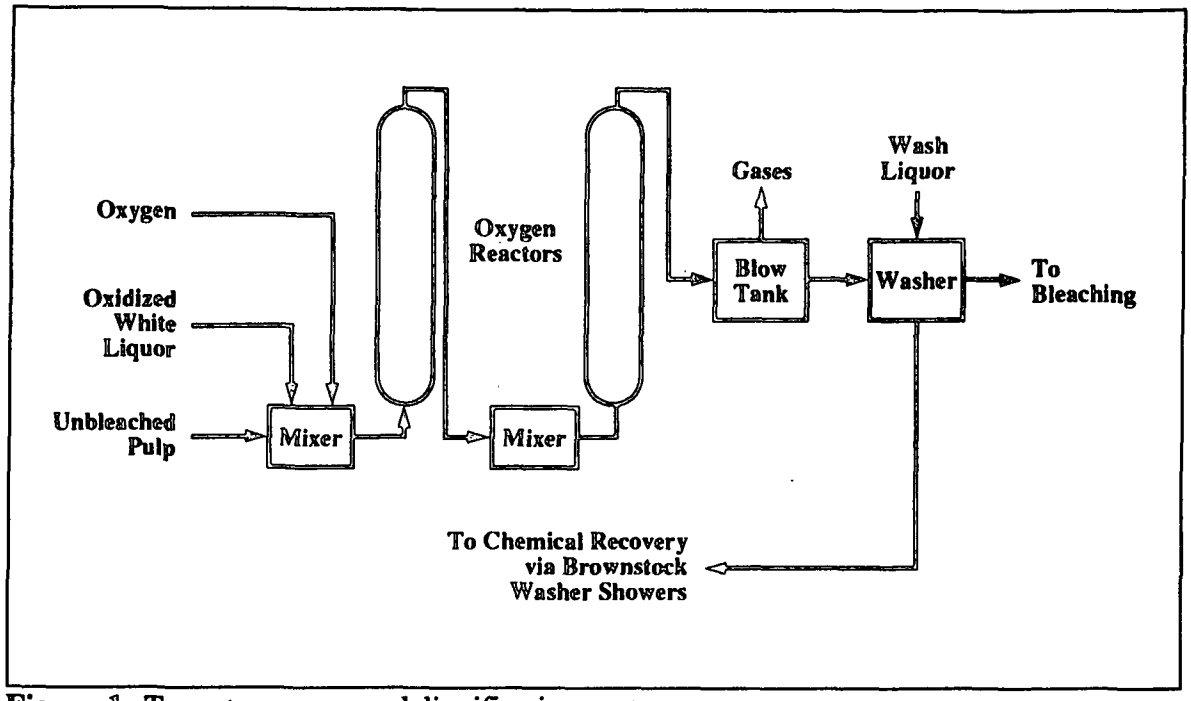

Figure 1 Two-stage oxygen delignification system

Enzyme Pretreatments

Exposing unbleached or oxygen delignified pulp to hemicellulases, in particular endoxylanases, facilitates lignin removal in subsequent stages. This effect may be due to disruption of xylan-mediated bonds between lignin and the fiber wall through xylan, to enhancement of lignin diffusion through pore enlargement, or both. Although not yet commercialized, the process has undergone successful mill trials[6]. Nonchlorine bleaching is also enhanced. Fully-bleached hardwood kraft can be made in the sequence X(EOP)D(EOP)D[7]. Hardwoods respond more

TABLE 1 SYMBOLS FOR TECHNOLOGY OPTIONS

Symbol	Definition
D	Chlorine dioxide
DD	Chlorine dioxide stages with an intermediate neutralization and wash
G	Green liquor treatment of bleach effluent
K	Extended kraft delignification
L	Open wash stage after leaching in storage
O	Oxygen delignification
P	Hydrogen peroxide
T	Chelating agent, usually EDTA
X	Pretreatment with hemicellulase enzyme such as xylanase
Z	Ozone
(D50C)	Mixture of chlorine dioxide and chlorine containing 50% chlorine dioxide
(D75C)	Mixture of chlorine dioxide and chlorine containing 75% chlorine dioxide
(DZ)	Chlorine dioxide followed by exposure to ozone with no intermediate washing
(EO)	Oxygen-reinforced caustic extraction
(EP)	Peroxide-reinforced caustic extraction
(EOP)	Caustic extraction reinforced with both oxygen and peroxide at elevated temperature and pressure
(HW)	Use of hardwood as raw material instead of softwood

favorably than softwoods, probably because of their greater xylan content. Active chlorine savings of 80-100% are possible for hardwoods, but savings of only 20-25% have been realized for softwoods.

Improved Pulp Washing

Carryover of dissolved solids from pulping or oxygen delignification into a (CD) stage has the undesirable effects of increasing chemical consumption and increasing the amount of chlorinated organic products formed. Compared to perfectly washed pulp, oxygen stage carryover amounting to 20 kg COD per ton of pulp can increase the consumption of active chlorine by 12 kg/t and the amount of AOX formed by 40%[8]. Carryover can be reduced to very low levels (about 5kg COD/t) by an open wash stage located downstream of a washed pulp storage tower. The storage period allows time for diffusion of dissolved organic material out of the fiber wall, and fresh wash water effectively removes it. Alternatively, two press washers in series will allow similarly low carryover levels to be achieved.

Chlorine Dioxide Delignification

Substitution of chlorine dioxide for a small fraction of the chlorine in the chlorination stage has been practiced for many years to prevent excessive pulp viscosity loss and associated strength losses. Substitution for larger fractions was also practiced by some mills to achieve reductions in effluent color and total chemical consumption[9]. Chlorine dioxide substitution also decreases the amount of chlorinated organic compounds formed during bleaching. A useful rule of thumb is that the amount of AOX formed is proportional to the amount of *atomic* chlorine consumed, whether the chlorine atoms are contained in chlorine molecules or chlorine dioxide molecules. The proportionality constant is such that 9-10% of the chlorine atoms applied end up as AOX[10]. Using chlorine dioxide instead of chlorine has a double-barreled beneficial effect on AOX formation because chlorine dioxide has about two and a half times the oxidizing power of chlorine and only half the content of chlorine atoms. At substitution levels of 50-70%, chlorine dioxide also delignifies more efficiently. At levels approaching 100% substitution, however, chlorine dioxide is distinctly less efficient than chlorine. When pure chlorine dioxide is used, the kappa factor (equivalent chlorine charged as percent of dry pulp weight divided by the kappa number of the entering pulp) must be about 35% higher than at 50% substitution[11].

Substitution of chlorine dioxide for all of the chlorine dioxide in the chlorination stage is currently the most technically feasible route to "chlorine-free" bleaching, also referred to as "elemental chlorine-free," molecular chlorine-free," and "chlorine gas-free" bleaching. Many mills now practice this part of the time and a few mills all of the time.

Peroxide Delignification

Hydrogen peroxide has often been viewed as a potential alternative to oxygen for delignification prior to chlorination and has been shown to be moderately effective when used in this way. Because of the high cost of peroxide relative to that of oxygen, however, this application of peroxide has remained, with one short-lived exception, confined to the laboratory. Recently, it has been shown that peroxide can be used to supplement an earlier oxygen stage, provided that

a relatively severe chelation step (using EDTA) is inserted between the two stages. The resulting process, called Lignox®, can raise the brightness of oxygen predelignified pulp to 70. This is one option for producing high-strength semibleached softwood pulp without the use of chlorine compounds. If the use of chlorine compounds is allowed, the brightness can be raised to 89 in the OTPD(EP)D sequence.

Ozone Delignification

Since ozone is one of the most powerful oxidizing agents known, it readily oxidizes and solubilizes residual lignin in kraft pulp. Because of its high reactivity, however, it must be used with extreme caution if pulp strength loss is to be avoided. This relatively low selectivity is one of several hurdles that ozone processes must overcome if they are to become widely commercialized. Others are potentially high operating costs, in part due to high electrical energy requirements, the need for elaborate ozone generation and oxygen decontamination systems, and potential scaleup difficulties associated with recycle of the effluent from the ozone stage. Nevertheless, the probability of widespread ozone use, though still debatable, is much higher than it was only a few years ago. The reasons are that the pressure to eliminate chlorine is now providing a greater driving force than in the past, and that one hurdle, being the first to try it on a commercial scale, is about to be removed. Union Camp Corporation will start up a 1000 ton per day high-consistency ozone delignification stage, part of an OZED sequence, later this year. The bleached pulp will be used to make paper in an integrated operation.

A gas phase (35-45% consistency) ozone delignification system is schematically represented in **Figure 2**[12]. Bleaching takes place at near-ambient conditions, so the reactor need not be pressurized. The system necessarily includes an upstream dewatering device as well as equipment for purifying, cooling, and drying oxygen recycled from the reactor to the ozone generator. This oxygen cannot be economically discarded because unconverted oxygen makes up about 90% of the volume of gas emerging from the ozone generator. It must be purified before being recycled to the generator because of contamination by products of the bleaching reaction. Ozone is similar to oxygen, in that the lignin and other organics dissolved during the reaction can, in principle, be recycled by evaporation and burning in the mill's pulping chemical recovery system. In the case of ozone, however, the effluent is acidic and contains dissolved metals that would normally be purged from the mill in the chlorination stage effluent. It will therefore be necessary to provide for part of the ozone stage effluent to be discharged from the system to prevent unacceptably high levels of metals buildup.

Uniformity of treatment is an important consideration in ozone bleaching because of the potential for loss of fiber strength due to locally high ozone concentration. Low-consistency systems are claimed to have an advantage in this regard. A recently developed low-consistency system has the additional advantage of eliminating the need for purification of recycled oxygen, as illustrated in **Figure 3**[13]. Its key feature is an absorption tower, where the freshly generated ozone is separated from unconverted oxygen by virtue of ozone's greater solubility in water. The oxygen leaving the absorption column, since it has not contacted the reacting mixture of pulp and ozone,

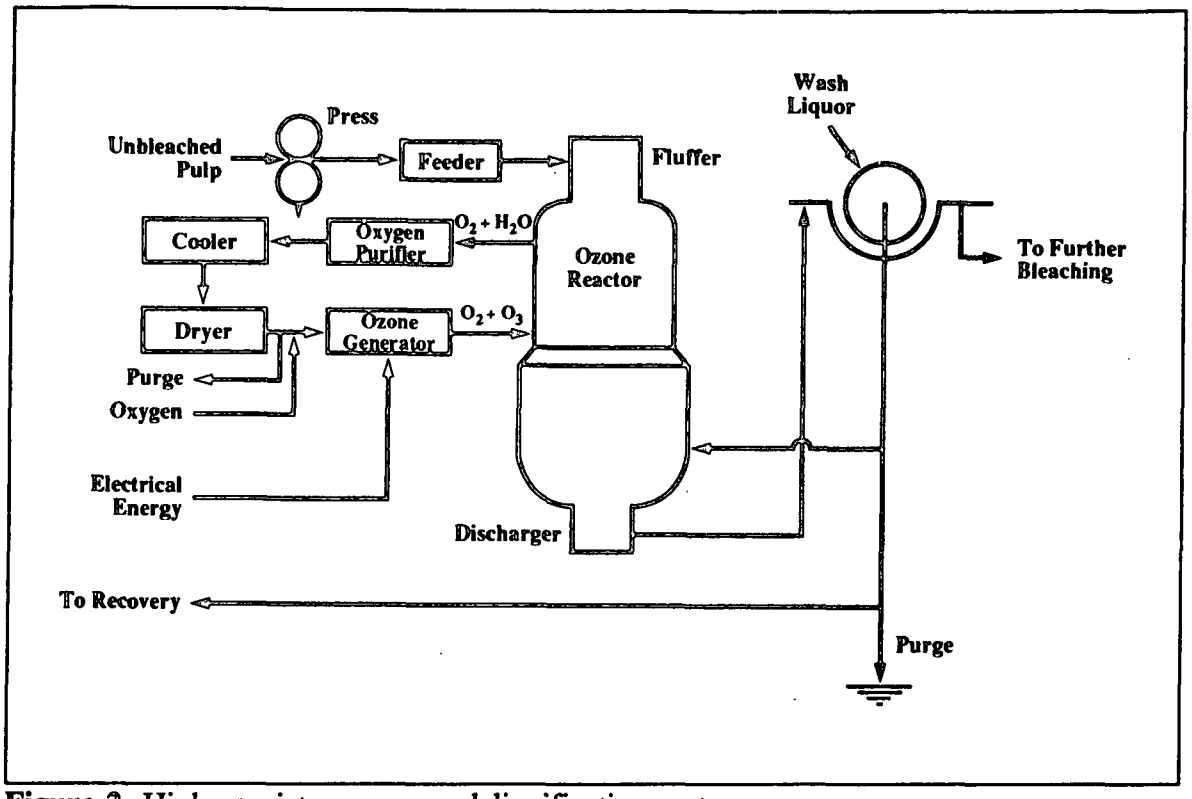

Figure 2 High-consistency ozone delignification system

remains uncontaminated by reaction products and needs only to be dried before being recycled to the ozone generator. To increase the ozone concentration in solution, the system is pressurized (up to 10 atm.) and maintained at as low a temperature as possible. This system is being developed in Austria in a 20 ton/day pilot plant.

Potential disadvantages of the low consistency approach include high mixing energy and high consumption of ozone by dissolved solids in the closed water circuit. In response to these disadvantages, medium-consistency systems have been designed and are undergoing further development. An example is the system installed on a semicommercial (120 tons/day) scale at Lenzing AG, also in Austria[14]. Essential features of these systems include a medium-consistency mixer and a compressor to reduce the volume of the oxygen-ozone feed stream. This is necessary because medium-consistency mixers do not operate satisfactorily when the gas content of the pulp stream is greater than 30% by volume. At Lenzing, beech magnesium bisulphite pulp is bleached in an (EOP)ZP sequence, an application in which the pulp entering the ozone stage has a very low kappa number (about 2), and both the ozone requirement and the degree of delignification are low (about 0.2% and 1 kappa unit, respectively). The feasibility of using medium-consistency ozone systems for bleaching kraft pulps, which would require a higher ozone charge than the Lenzing pulp, is currently being investigated in several 3-5 ton/day pilot plants[15,16].

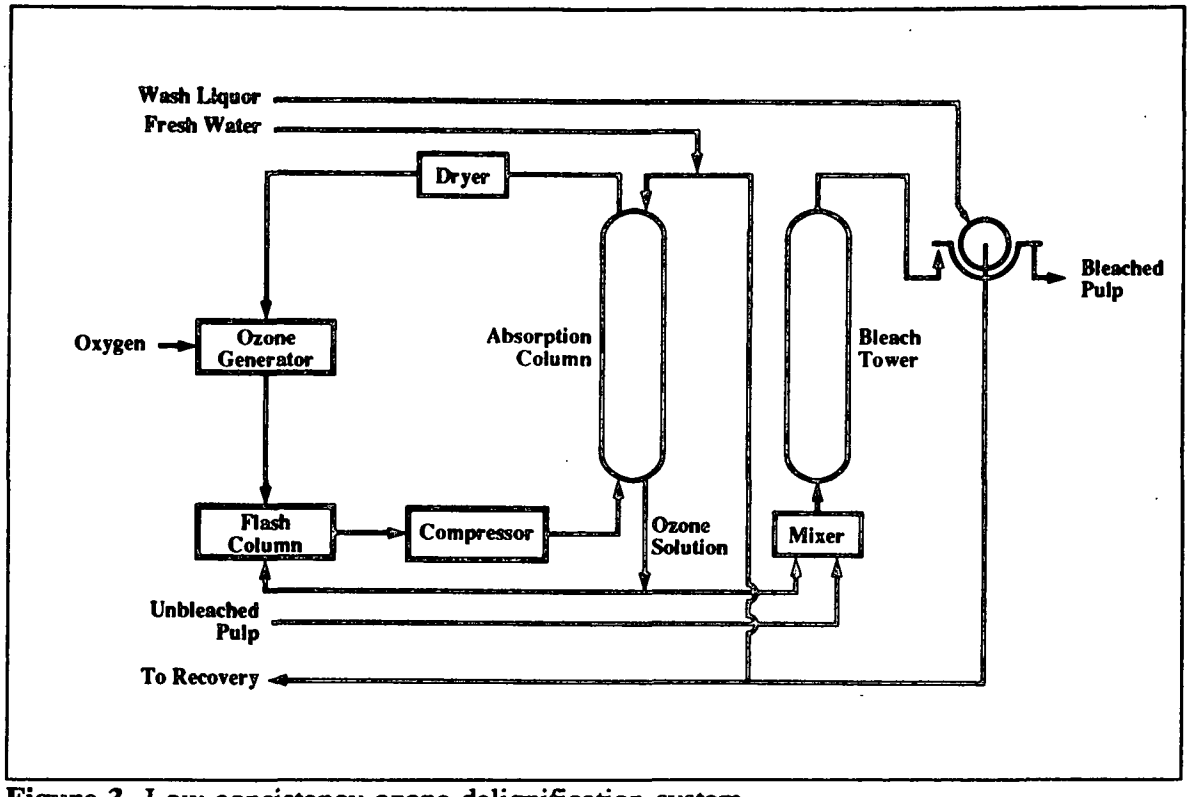

Figure 3 Low-consistency ozone delignification system

Commercial ozone bleaching systems will deal with the cost and selectivity problems by choosing sequences that require relatively low ozone charges. One likely result is that the ozone stage will be preceded by an oxygen stage, in which a substantial part of the lignin can be removed more cheaply. Another possibility is that ozone will be used in close conjunction with chlorine dioxide, in a (DZ) stage[17] for example. Chlorine dioxide, added 20-120 seconds before ozone, decreases the charge and increases the selectivity of the ozone.

Intense Oxidative Extraction

Addition of oxygen to the first caustic extraction stage, immediately following chlorination, became widespread during the early 1980s. The resulting gain in effectiveness of the extraction stage allowed a significant reduction in the charge of bleaching chemicals in subsequent stages. Shortly thereafter, as it became more desirable to limit the amount of chlorine applied in the first stage, it was realized that oxidative reinforcement could also be used to achieve this goal. Subsequently, it was shown that addition of hydrogen peroxide and increases in the time, temperature, and pressure of the oxidative extraction stage enhanced the degree to which the chlorine charge could be reduced without affecting the final bleaching result[18]. This tactic has become an important weapon in the arsenal of process engineers intent on generating less AOX. Decreases of 20-25% in kappa factor are possible.

Chemical Destruction of AOX

Organic chlorine compounds in bleaching effluents, particularly those from acidic stages such as chlorination and (DC) stages are susceptible to being converted to inorganic chloride by treatment with alkali. This can be exploited by sequence modifications, such as eliminating washing before the caustic extraction stage[19] or by posttreatment of effluent streams. The effectiveness of posttreatment is considerably enhanced by the presence of sulfide or hydrosulfide in the alkali used. This observation is the basis for the development of a process for AOX destruction by treatment with kraft green liquor[20]. AOX reductions of 30-40% are achieved, including a 10% reduction from simply neutralizing the acid effluent.

An effluent treatment process based on treatment with ozone and hydrogen peroxide is under development; AOX reductions of about 30% appear possible[21].

AOX Reduction in Biological Treatment Systems

AOX reductions of about 30% are often observed during secondary treatment in aerated stabilization basins, and higher reductions, about 50%, in activated sludge systems[22]. It is unlikely that removal rates can be increased, since the remaining AOX probably consists of polymeric material of a molecular size that is too great to be ingested by the microflora found in these systems.

PROCESS SCENARIOS

In attempting to predict what the bleaching process will look like in the year 2000, it is necessary to make some assumptions about the milieu the industry will find itself in at that time. As outlined in the introduction, that milieu can be described in terms of various issues: environment, energy, product specialization, etc. Given current events, it seems likely that the environmental issue will dominate, so the scenarios given here are distinguished on that basis. Furthermore, recognizing that AOX is likely to be given more emphasis than it deserves by both the public and regulatory agencies, the scenarios are defined in terms of that sum parameter, unsatisfactory though it may be.

A variety of combinations of the technology options described above were evaluated by calculating for each the expected level of AOX discharge into the receiving water. All sequences were assumed to discharge their effluents into a secondary treatment system where neutralization reduces AOX by 10% and biological activity reduces it by a further 20% of the influent value. Other assumptions concerning AOX reductions are as outlined in the above reviews of individual technologies. Additivity was assumed throughout. The results were used to classify these technology combinations into candidate processes for the various AOX limitation scenarios.

Scenario 1: AOX Limited to 1.5 kg/t

As already mentioned, a very good scientific case can be made for the acceptability and sustainability of AOX discharges which are greater than 1.5 kg/t. Assuming that this argument prevails and a 1.5 kg/t limit is accepted, a variety of process options may be considered. All will produce nontoxic effluents that do not contain any detectable chlorinated dioxins or furans, and all will produce very low, presumably acceptable, levels of chloroform. All employ reduced or nonexistent levels of elemental chlorine, and all are presumed to discharge their effluents via a secondary treatment system. Some such options are listed in Table 2.

The first, and the simplest, involves replacing all of the chlorine in the chlorination stage with chlorine dioxide. Alternatively, enzyme pretreatment, intense oxidative extraction, or green liquor effluent treatment would allow the total active chlorine charge to be reduced to the point where 25% chlorine could be tolerated without exceeding the AOX limit. Simultaneous use of any two of these three additional technologies would allow the proportion of elemental chlorine to be increased to 50%. The use of 50% chlorine would also be enabled by using extended delignification or oxygen delignification or if hardwood were the raw material instead of softwood.

TABLE 2 SOME BLEACHING TECHNOLOGIES PREDICTED TO DISCHARGE LESS THAN 1.5 KG/T AOX

D(EO)DD	X(D50C)(EO)DD + G
X(D75C)(EO)DD	(D50C)(EOP)DD + G
(D75C)(EOP)DD	O(D50C)(EO)DD
(D75C)(EO)DD + G	K(D50C)(EO)DD
X(D50C)(EOP)DD	(D50C)(EO)DD (HW)

Scenario 2: AOX Limited to 0.5 kg/t

In the event that it becomes necessary to limit AOX discharges to values of 0.5 kg/t or less, more extensive changes will be necessary and costs will be higher. Some options for softwood pulp production are listed in **Table 3.** A combination of enzyme pretreatment, 100% substitution, intense oxidative extraction, and chemical treatment of effluent would be one; another would be oxygen delignification followed by the (DZ)ED sequence. Oxygen delignification would also allow the AOX constraint to be met by a combination of (a) enzyme pretreatment and 100% substitution, (b) 100% substitution and intense oxidative extraction, (c) 100% substitution and chemical treatment of effluent, or (d) enzyme pretreatment, 75% substitution, intense oxidative

extraction, and chemical treatment of effluent. The same combinations may also be expected to work if extended delignification (to a kappa number below 20) is substituted for oxygen delignification. Using both extended delignification and further delignification in an oxygen stage would enable (a) use of a D(EO)DD sequence, (b) decreasing the substitution to 75% and chemically treating the effluent, (c) decreasing the substitution to 75% in conjunction with an enzyme pretreatment, or (d) decreasing the substitution to 50% and using both an enzyme pretreatment and chemical effluent treatment.

TABLE 3 SOME SOFTWOOD BLEACHING TECHNOLOGIES PREDICTED TO DISCHARGE LESS THAN 0.5 KG/T AOX

XD(EOP)DD+G	OXD(EO)DD	KXD(EO)DD	KOD(EO)DD
O(DZ)(EO)D	OD(EOP)DD	KD(EOP)DD	KO(D75C)(EO)DD+G
OZ(EO)D	OD(EO)DD+G	KD(EO)DD+G	KOX(D75C)(EOP)DD
OTPD(EP)D	OX(D75C)(EOP)DD+G	KX(D75C)(EOP)DD+G	KOX(D50C)(EOP)DD+G

Hardwoods, being more readily delignified than softwoods, offer a greater variety of options for meeting the 0.5 kg AOX constraint. Some are listed in Table 4. Using a 100% chlorine dioxide first stage should allow the AOX target to be met by implementing any one of four additional options: an open wash stage, a hemicellulase pretreatment, intense oxidative extraction, or green liquor posttreatment of effluent. A combination of any two of these would allow the substitution level to be decreased to 75%, and using the last three together would permit the use of 50% chlorine.

TABLE 4 SOME BLEACHING TECHNOLOGIES FOR CONVENTIONAL HARDWOOD PULP PREDICTED TO DISCHARGE LESS THAN 0.5 KG/T AOX

LD(EO)DD	X(D75C)(EOP)DD
XD(EO)DD	(D75C)(EOP)DD + G
D(EOP)DD	X(D50C)(EOP)DD + G
D(EO)DD + G	X(EOP)D(EOP)D

Reducing the kappa number of the unbleached pulp by either extended delignification or oxygen delignification would expand the range of choices. Some are listed in Table 5. A first stage of

100% chlorine dioxide would require no additional measures, and using any one of the four additional measures referred to above would allow the substitution level to be decreased to 75%. It could be further reduced, to 50%, by using intense oxidative extraction together with either enzyme pretreatment or chemical posttreatment of effluent.

As shown in Table 6, using both extended delignification and oxygen delignification on hardwoods should allow the 0.5 kg/t AOX target to be met at 75% substitution or, by using any one of the four technologies mentioned above, at 50% substitution.

TABLE 5 SOME BLEACHING TECHNOLOGIES FOR HARDWOOD PULP PREDICTED TO DISCHARGE LESS THAN 0.5 KG/T AOX AFTER EXTENDED DELIGNIFICATION OR OXYGEN DELIGNIFICATION

D(EO)DD	(D75C)(EO)DD) + G
L(D75C)(EO)DD	X(D50C)(EOP)DD
X(D75C)(EO)DD	(D50C)(EOP)DD + G
(D75C)(EOP)DD	

TABLE 6 SOME BLEACHING TECHNOLOGIES FOR HARDWOOD PULP PREDICTED TO DISCHARGE LESS THAN 0.5 KG/T AOX AFTER BOTH EXTENDED DELIGNIFICATION AND OXYGEN DELIGNIFICATION

(D75C)(EO)DD	(D50C)(EOP)DD
L(D50C)(EO)DD	(D50C)(EO)DD + G
X(D50C)(EO)DD	

Scenario 3: AOX Limited to 0.1 kg/t and Scenario 4: Chlorine Compounds Disallowed

Under these scenarios the selection of bleaching process alternatives becomes seriously limited. Combining all of the technologies discussed above may allow hardwood pulp to be fully bleached under the 0.1 kg AOX constraint, but the capital costs involved would be prohibitively high. A softwood kraft, after both extended delignification and oxygen delignification, has been successfully bleached in the sequence (DZ)(EOP)DD by Dillner and Tibbling[23] with the production of only 0.2 kg/t AOX. Assuming that this effluent would respond well to a combination of chemical treatment and activated sludge treatment, it would allow the 0.1 kg target to be met.

Under the scenario where chlorine compounds are prohibited, it seems unlikely that it will be possible to maintain today's pulp quality standards. The closest approach would be provided by the sequence OZEPY (Y=hydrosulfite) after extended delignification[24].

TABLE 7 SOME BLEACHING TECHNOLOGIES FOR HARDWOOD PULP PREDICTED TO DISCHARGE LESS THAN 0.1 KG/T AOX AFTER BOTH EXTENDED DELIGNIFICATION AND OXYGEN DELIGNIFICATION

KOLXD(EOP)DD + G (HW)	KOZEPY
KO(DZ)(EOP)DD + G	

CONCLUSION

Interactions among various driving forces and resistances will determine the nature of the bleach plant of the year 2000. The most prominent among these are regulatory and market pressures on environmental parameters on one hand and economic realities on the other. AOX, although not useful as a predictor of environmental impact, is an environmental parameter that will very probably have a strong influence on future bleaching process choices. Several technologies are available to reduce AOX, and cost considerations aside, they can be combined in various ways to give more or less additive effects. If AOX is limited to a value of 1.5 kg/t, a variety of options are available, all involving replacement of chlorine with chlorine dioxide to an extent depending on the extent to which other technologies are also used. More severe limitations on AOX will further limit the available options. Complete prohibition of the use of chlorine compounds would force a reduction in bleached pulp quality standards.

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